**Abstract**

**DETERMINATION OF ORGANOPHOSPHORUS PESTICIDE RESIDUES IN PEPPER AND SOIL** **FROM EDOZHIGI, GBAKO LGA, NIGER STATE**

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**ABSTRACT**

This study was carried out to determine the concentration of organophosphorus pesticide residues in composite samples of scotch bonnet pepper and soil from Edozhigi, Gbako Local Government, Niger State. Modified QuEchERS method was used for the extraction. The concentrations of the pesticides were determined by gas chromatography-mass spectroscopy (GC-MS). The concentration of 0.060, 0.011, 0.004, 0.044, 0.022, 0.006, 0.255, 0.062, 0.096 mg/kg were obtained for Diazinon, Chlorpyrifos-Methyl, Pirimiphos – Methyl, Fenitrothion, Chlorpyrifos, Chlorfenvifos, Fenamiphos, Triazophos, and Azinfos - Methyl respectively. While for the soil the values obtained were 0.035, 0.046, 0.099, 0.016, 0.053, 0.061, 0.081 mg/kg for Dimethoate, Fenitrothion, Malathion, Chlorpyrifos, Ethion, Triazophos, Azinfos – Methyl respectively. The obtained values when compared with Codex Maximum Residue levels, were found to be below the Maximum Residue Limits (MRLs). The concentration of the detected pesticides in pepper were observed to be below the FAO/WHO maximum residue permissible limits of Diazinon (0.10 mg/kg), Chlorpyrifos-Methyl (0.30 mg/kg), Pirimiphos – Methyl (0.05 mg/kg), Fenitrothion (0.80 mg/kg), Chlorpyrifos (0.30 mg/kg), Chlorfenvifos (0.30 mg/kg), and Azinfos – Methyl (1.00mg/kg), except for Fenamiphos (0.03 mg/kg) and Triazophos (0.05 mg/kg), whose values are slightly above the stated permissible limits for the pesticides. Although, there is an indication that the pepper from the farms is safe for consumption and therefore may pause little or no health threat to humans but there is need for strict adherence to good agricultural practices (GAP), to avoid bioaccumulation and in the long run it’s negative effects on living things. However, periodic monitoring of the pesticide’s application and the determination of the chemical residue is recommended

**Key Words**: organophosphorus, pepper, soil, transfer factor

I. INTRODUCTION

Pepper production is a key sector of the Nigeria economy. It contributes a significant percentage of the Gross Domestic Product (GDP) and contributes to the total spicy needs of the country, provides source of raw materials for the industries and an easy market for industrial products like pesticides, fertilizers, equipment and machinery. The importance of spice products in the human diet especially in the tropical Africa and other countries are the reasons for the pool of money being injected by many countries in the tropic into the cultivation of pepper (Ogwu *et al.*, 2018)

Nigeria has been recognized to be one of the countries that are involved in the cultivation of these crops. However, an important source of concern to the farmers and agricultural sector at large is the pests. Pests are either plants or animals that feed on either the leaves, flowers, grains or fruits of other plants thereby causing damage to them and making them unavailable for human consumption (World Health Organization, 2020). During crop cultivation, chemicals have been used to protect them against the harmful impacts of pests, pathogens and weeds (Fried *et al.*, 2017). In Nigeria, pepper cultivation involves the use of pesticides on a large scale. These chemicals are used on vegetables such as pepper, yet there has not been keen attention on the safety of the use of the pesticide because the vast majority of farmers in Nigeria lacks the proper training on the use and management of pesticides (Marete *et al.*, 2021). However, except in other parts of the country, there is no published data on organophosphorus pesticide residues contamination in cultivated Pepper in Gbako.

Organophosphorus accounts for almost 34% of the pesticides produced and sold for agricultural purpose worldwide (Ning *et al.*, 2021). Their excessive and uncontrolled usage causes pollution to the environment. They also have toxic effects on plants and animals which have ripple effect on the agricultural yield and productivity (Chawla *et al.*, 2018; Fu *et al.*, 2022). The toxicity of organophosphorus pesticides depends on the amount of sulfur present and the valency of the phosphorus (Chen *et al.*, 2021). Though, phosphorus is always present in organophosphorus pesticides but there is a group where oxygen has replaced sulfur (oxon pesticide). The oxon has P = O bond instead of P = S (thion) that is present in most organophosphorus pesticides. Most of the organophosphorus pesticides are simply the esters of phosphoramidic acid, phosphonic acid or phosphoric acid with aryl or alkyl attachments and the side chains or leaving groups (Murtadha, 2020). They are often classified based on their leaving group as heterocyclic, phenyl and aliphatic (Sarlak *et al.*, 2021). Organophosphorus pesticides have ability to translocate from the root to the leaves of some plants. Example of such plant is Phragmites australis where the concentration of the organophosphorus pesticides in their leaves were more than what was found in the root and the stems (Olisah *et al.*, 2021). Based on the environmental, health and economic importance of organophosphorus compounds, it is important to thoroughly look into their impacts, how they can be detected in various environmental samples and methods of removing them. This is to minimize the impact of these pesticides on man and the environment (Ajiboye *et al.*, 2022).

II. MATERIALS AND METHODS

**Reagents**

Solvent, reagents and pesticides standard were of analytical grade and obtained from sigma and Co. The glass wares were cleaned with detergent and water, raised with distilled water and acetonitrile before used. Centrifuge and Gas chromatograph couple with mass spectrometer detector (GC-MS) are used for the extraction and analysis respectively.

**Sample collection**

Fresh Pepper and soil samples were collected from three major farms from Edozhigi, Niger state. The sample were mixed to make a composite of each of the pepper and soil from the farms, transported to the laboratory in a clean black polythene bag and kept in the refrigerator.

**Samples extraction**

QuEchERS was used for sample preparation as describe by (Momoh *et al.*, 2020).

The samples were grinded to homogenized and increase the surface area. 15 g of homogenized sample was weighed into a cleaned 50 Cm3 test tube; 15 Cm3 of acetonitrile was measured and added to the sample and shake vigorously for 5 minutes. This was done to ensure the organic pesticides residues were dissolved in the solvent and separated from water. 6g of MgSO4 and 1.5 g NaCl were added to remove the water and maintained the polarity respectively, before centrifuge for 10 minutes at 600 rpm. The supernatant was transferred into cleaned test tube followed by the addition of 150 mg of MgSO4 and shake for 30 seconds and centrifuge for 1minute at 150 rpm, the cleared extract was used for GC-MS analysis. The process was carryout in all the samples and control.

III. INSTRUMENTATION

The analysis was carryout at Nigeria institute of Oceanography and Marine Research (NIOMR), Lagos State Using GC-MS model 7890 Agilent technologies, equipped with auto sampler, capillary column length HP 5ms of length 30m and internal diameter of 0.320mm and 0.25 micrometer. The temperature was program at 60OC held for 5minutes at 8OC per minute to the final temperature of 300OC held for 30 seconds and the MSD transfer line was held at 300OC. Split injection of one microliter was carried out at 300 oC injector temperature with a purge flow of 3 ml/minute, the carrier gas used was helium, with flow rate of 2.17 ml/minute and the pressure was 150 kpa. The interface temperature was 300 oC. The mass spectrometer model 5975 Agilent technologies ionization mode was electron impact with ion sources temperature of 230OC and in full scan mode ranges from 45-500M/Z.

Internal standard technique was employed to analyze the fresh Pepper and soil extracts. The organophosphorus standard used are Dimethoate, Diazinon, Chlorpyrifos- methyl, Pirimiphos – methyl Fenitrothion, Malathion, Chlorpyrifos, Chlorfenvifos, Fenamiphos, Ethion, Triazophos, Azinfos – methyl, Dichlorvos, Carbofuran, Mevinfos, Etrimfos, Pirimicarb, Diclofenthion, Metribuzin, Fenthion, Bromophos-methyl and Bromophos-ethyl. The standards were prepared in different concentrations from 0.100 ppm to 2.00 ppm and was used to generate calibration curves for each compound.

IV. RESULTS AND DISCUSION

The retention times of the analytes detected in the samples were the same as those of standards and the spectra has a very high match factor. Table 1 Show the concentration of organophosphorus pesticides residue in the fresh pepper and soil extract. Almost all the OPPs determined in the samples are below the maximum Residual limit However the concentration increased significantly above the MRL in pepper sample for Fenamiphos, while Diazinon, Chlorpyrifos- methyl, Pirimiphos – methyl, Chlorfenvifos and Fenamiphos are below the limit of detection in the soil extracts. Twenty-two OPPs standards were used for analysis as shown in table I and twelve OPPs; Dimethoate, Diazinon, Chlorpyrifos- methyl, Pirimiphos – methyl, Fenitrothion, Malathion, Chlorpyrifos, Chlorfenvifos, Fenamiphos, Ethion, Triazophos and Azinfos – methyl was determined in fresh pepper and soil samples extract as shown in table 1. Fenamiphos, while Diazinon, Chlorpyrifos- methyl, Pirimiphos – methyl, Chlorfenvifos and Fenamiphos are below the limit of detection in the soil sample extracts, this may attribute to the volatility nature of the OPPs residues as reported by (Momoh *et al.*, 2020).

Most of the organophosphorus pesticide residues detected in the fresh pepper extract was also reported in a work of (Sidhu *et al.*, 2019), (Kaushal *et al.*, 2021), (Salihu *et al.*, 2023), (Shim *et al.*, 2023), (Fatunsin *et al.*, 2020). This indicates that farmers may lack information about the possible health risk of OPPs residues in the food spices and the hazard to the environments. The frequent application could be as a result of the availability and low cost of these class of chemicals as reported by (Cousins *et al.*, 2019; Rani *et al.*, 2021).

**Transfer from soils to pepper**

Soil to crop transfer is one of the major components of human exposure to pesticides through food chain. Transfer factor (TF) or plant concentration factor (PCF) is a parameter used to describe the transfer of chemicals elements from soil to plant (Neina and Science, 2019). In this study, the values of the transfer factors of different pesticide from soil to pepper are also presented in Table 1. The trend of TF for pesticide detected in pepper samples studied were in order: chlorpyrifos>Azinfos-methyl>Triazophos>Fenitrothion. The mobility of chemical residues from soil to plants is majorly a function of the physical and chemical properties of the soil and of crop varieties and could be changed by a number of environmental and human factors such as climate change, water contamination, and changes in water runoff, snowpack, ground water, and light regims (Vatanpour *et al.*, 2020). The TF values range from 1.375 and 0.957, the least and highest are for Azinfos-methyl and Fenitrothion respectively.

**TABLE 1. Detectable and non- detected OPPs residues in fresh pepper and soil (mg/kg)**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **OPs** | **Soils** | **Pepper**  |  **T/F** | **MRL (mg/kg)** |
| Dimethoate | 0.035 | ND | 0 | 0.20 |
| Diazinon | ND | 0.060 | 0 | 0.10 |
| Chlorpyrifos- methyl | ND | 0.011 | 0 | 0.30 |
| Pirimiphos – methyl | ND | 0.004 | 0 | 0.05 |
| Fenitrothion | 0.046 | 0.044 | 0.957 | 0.80 |
| Malathion | 0.099 | ND | 0 | 0.50 |
| Chlorpyrifos | 0.016 | 0.022 | 1.375 | 0.30 |
| Chlorfenvifos | ND | 0.006 | 0 | 0.30 |
| Fenamiphos | ND | 0.255 | 0 | 0.03 |
| Ethion | 0.053 | ND | 0 | 0.30 |
| Triazophos | 0.061 | 0.062 | 1.016 | 0.05 |
| Azinfos – methyl | 0.081 | 0.096 | 1.185 | 1.00 |
| Dichlorvos | ND | ND | 0 | 0.20 |
| Carbofuran | ND | ND | 0 | 0.05 |
| Mevinfos | ND | ND | 0 | 0.20 |
| Etrimfos | ND | ND | 0 | 0.20 |
| Pirimicarb | ND | ND | 0 | 0.50 |
| Diclofenthion | ND | ND | 0 | 0.20 |
| Metribuzin | ND | ND | 0 | 0.20 |
| Fenthion | ND | ND | 0 | 0.20 |
| Bromophos-methyl | ND | ND | 0 | 0.30 |
| Bromophos-ethyl | ND | ND | 0 | 0.30 |

KEY: ND = Not detected, T/F = Transfer factor, MRLs = Maximum residue limit, OPs = Organophosphorus.

**CONCLUSION**

The result obtained from the present study shows that organophosphorus pesticide residues are present in the fresh pepper and soil from selected farmland in Edozhigi, Gbako Local Government, Niger State, are Dimethoate, Diazinon, Chlorpyrifos- methyl, Pirimiphos – methyl, Fenitrothion, Malathion, Chlorpyrifos, Chlorfenvifos, Fenamiphos, Ethion, Triazophos and Azinfos – methyl with concentration of the Fenamiphos and Triazophos whose values are slightly above the MRL setup by FAO/WHO. The concentration of OPPs residues in soil samples are below the maximum residual limit. The Dimethoate, Fenitrothion, Malathion, Chlorpyrifos, Ethion, Triazophos and Azinfos – Methyl respectively. The study also provides data on organophosphorus pesticide residues in the fresh pepper sample which shows slight increase in concentrations of the residues. Although, there is an indication that the pepper from the farmlands are safe for consumption and therefore may pause little or no health threat to humans but there is need for strict adherence to good agricultural practices (GAP), in order to avoid bioaccumulation and in the long run, its negative effects on both human and the environment. However, periodic monitoring of the pesticides application and the determination of the chemical residue is recommended. Strict regulation and public awareness are also required by regulatory agency to educate the users on the health risk and environmental effect.

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